The Carbon Cycle

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1. Introduction

Carbon is an important element in our planet. From the food we eat to the energy that fuels our transportation is made up of carbon. It comes in numerous structures, but one of the most important forms that carbon takes is of its oxide called *carbon dioxide*.

Carbon dioxide (CO_2) is a gas in the atmosphere made up of one carbon atom and two oxygen atoms arranged in a linear structure as shown in Figure 1. Its first observations were made during the 17th century by the Flemish chemist Jan Baptist van Helmont and its properties were studied more thoroughly in the 1750's by the Scottish physicist and chemist Joseph Black.

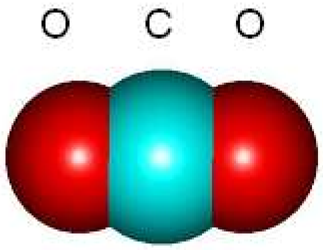

Figure 1. Carbon Dioxide Structure

Carbon dioxide plays an essential role in one of many exchanges of substances between living organisms (biosphere), the land (geosphere), the water (hydrosphere) and the air (atmosphere). This exchanges or interactions are called *biogeochemical cycles*. The biogeochemical cycle, which involves carbon, is called *the carbon cycle*.

The carbon cycle is therefore important to life and the proper knowledge of the processes involved in it is essential. This knowledge can then be used to see the effects of anthropogenic activities to the environment. A good example of this is the continued and dramatic increase of atmospheric carbon dioxide due to human influence. Seeing these effects would enable us to undergo changes and begin measures to change our consumption and emission of carbon dioxide through new laws and improved protocols.

2. Basic Concepts

Living organisms, the land, the water and the air act as reservoirs or forms in which carbon resides in the Earth. More specifically, these are the atmosphere (denoted as A), terrestrial biosphere (denoted as T; including freshwater systems), oceans and sediments (denoted as S and D, respectively; includes fossil fuels). Quantitatively, the reservoirs or sometimes termed as *burdens* may be expressed in terms of the *mass of carbon* (represented by M) as Gigatons-carbon (Gt C) or as Petagrams-carbon (Pt C). The exchanges between these reservoirs and the processes involved, called *transfer mechanisms*, may be expressed in terms of the *transfer rate* or *flux* in units of Petagrams-Carbon per year (Pt C / yr). Another important quantity involved in the carbon cycle is the *residence time or renewal time* (represented by τ_o). The residence time for carbon in a reservoir is estimated by dividing the amount of carbon in that reservoir by the transfer rates in (*source*, Q) and out (*sink*, S) of it. The relationships between these quantities can be written as

$$\tau_o = \frac{M}{S} \tag{1}$$

In block diagram form these quantities are depicted in Figure 2. The flux out of the reservoir is related to the amount of carbon in the reservoir as

$$S = kM \tag{2}$$

where k is called the *time constant*. Figure 3 shows specific reservoirs and transfer rates.

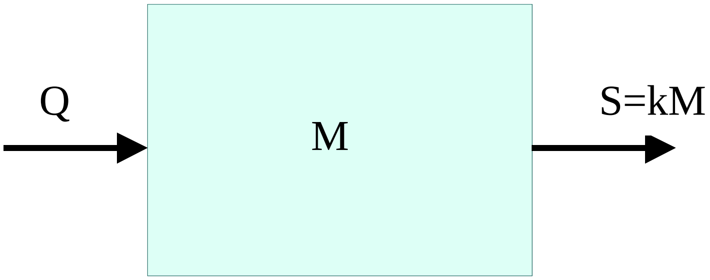

Figure 2. Block Diagram of Sources, Reservoirs and Sinks

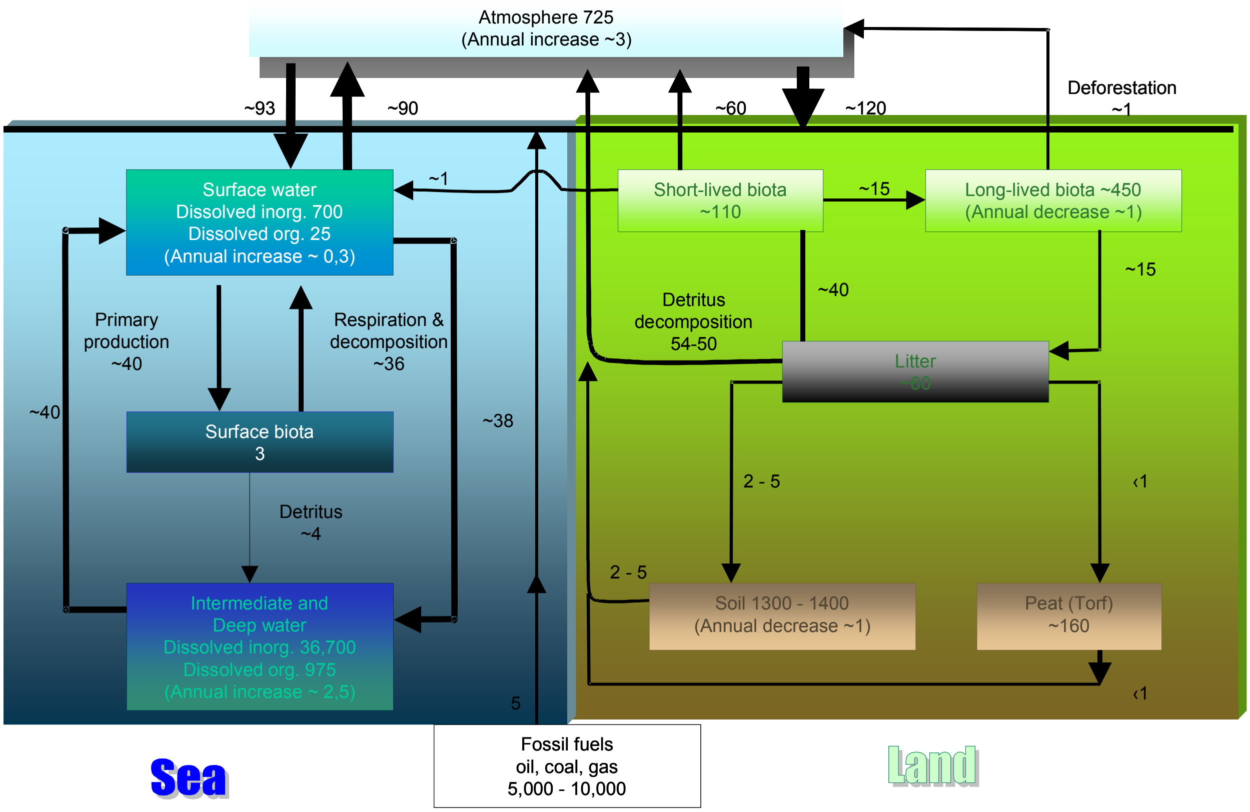

Figure 3. Reservoirs and Fluxes in the Carbon cycle. (Units are 10^{15} Pg C (burdens) and Pg C / yr (fluxes)).

The rate of change of the content of a reservoir is expressed as

$$\frac{dM}{dt} = Q - S = \frac{M}{\tau_o} \tag{3}$$

The adjustment process towards an equilibrium condition from an initial situation is given by

$$\frac{dM}{dt} = Q_1 - S = Q_1 - kM \tag{4}$$

If the initial condition is $M(t=0) = M_o$, the solution to equation (4) would then be

$$M(t) = M_1 - (M_1 - M_o)e^{-kt} \tag{5}$$

Graphically, equation (5) is shown in Figure 4. The *response time*, τ_{cycle} is given by

$$\tau_{cycle} = \frac{1}{k} \tag{6}$$

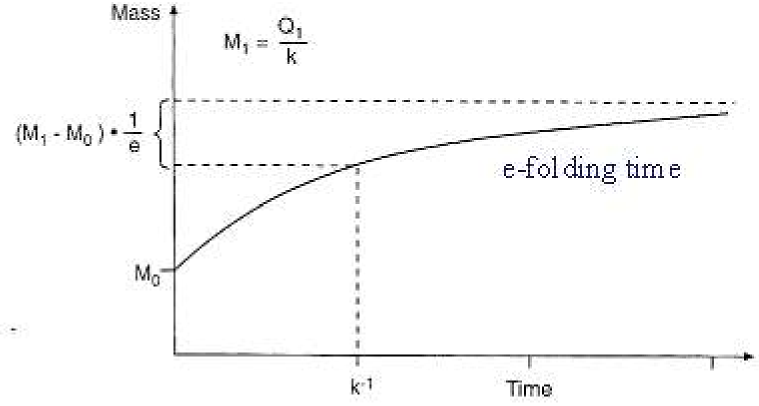

Figure 4. Exponential Adjustment Process

The above descriptions are a highly ideal case. Reservoirs are in fact coupled to one another. The flux, F_{ij} from one reservoir i to another reservoir j is expressed as

$$F_{ij} = k_{ij} M_i \tag{7}$$

The variation in time of the amount of carbon M_i in reservoir i is given by

$$\frac{dM_i}{dt} = \sum_{j=1}^{n} k_{ji} M_j - M_i \sum_{j=1}^{n} k_{ij} \quad for\ j \neq i \tag{8}$$

where n is the total number of reservoirs in the system. In matrix form, these differential equations may be written as

$$\frac{d\overline{M}}{dt} = \bar{k}\overline{M} \tag{9}$$

In statistical physics, equation (9) is called the *master equation*. Here, $\overline{M}$ is a vector with elements

$$\begin{bmatrix} M_1 \\ M_2 \\ \vdots \\ M_n \end{bmatrix} \tag{9}$$

and ***k*** are linear combinations of the coefficients k_{ij}. An example of a simple coupled reservoir system is shown in Figure 5. It can be seen that the fluxes are proportional to the content of the emitting reservoirs. The response time for this system is expressed as

$$\tau_{cycle} = \frac{1}{k_{12} + k_{21}} \tag{10}$$

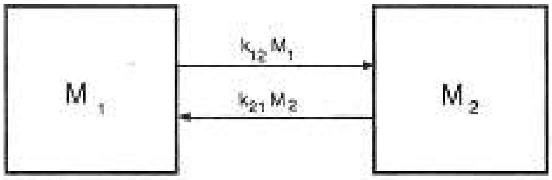

Figure 5. A Coupled Two-Reservoir System

The residence time or renewal time for each reservoir is given by

$$\tau_{oi} = \frac{M}{S_i} \tag{11}$$

The *turnover times* of the two reservoirs are therefore related with the renewal times of each reservoir through

$$\frac{1}{\tau_{cycle}} = \frac{1}{\tau_{o1}} + \frac{1}{\tau_{o2}} \tag{12}$$

A more complicated coupled reservoir system is shown in Figure 6. Figure 7 depicts a simplified carbon cycle model.

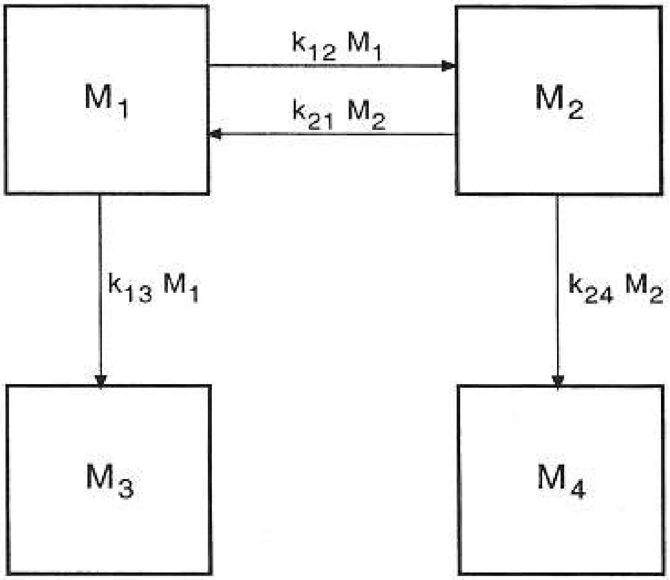

Figure 6. A Coupled Four-Reservoir System

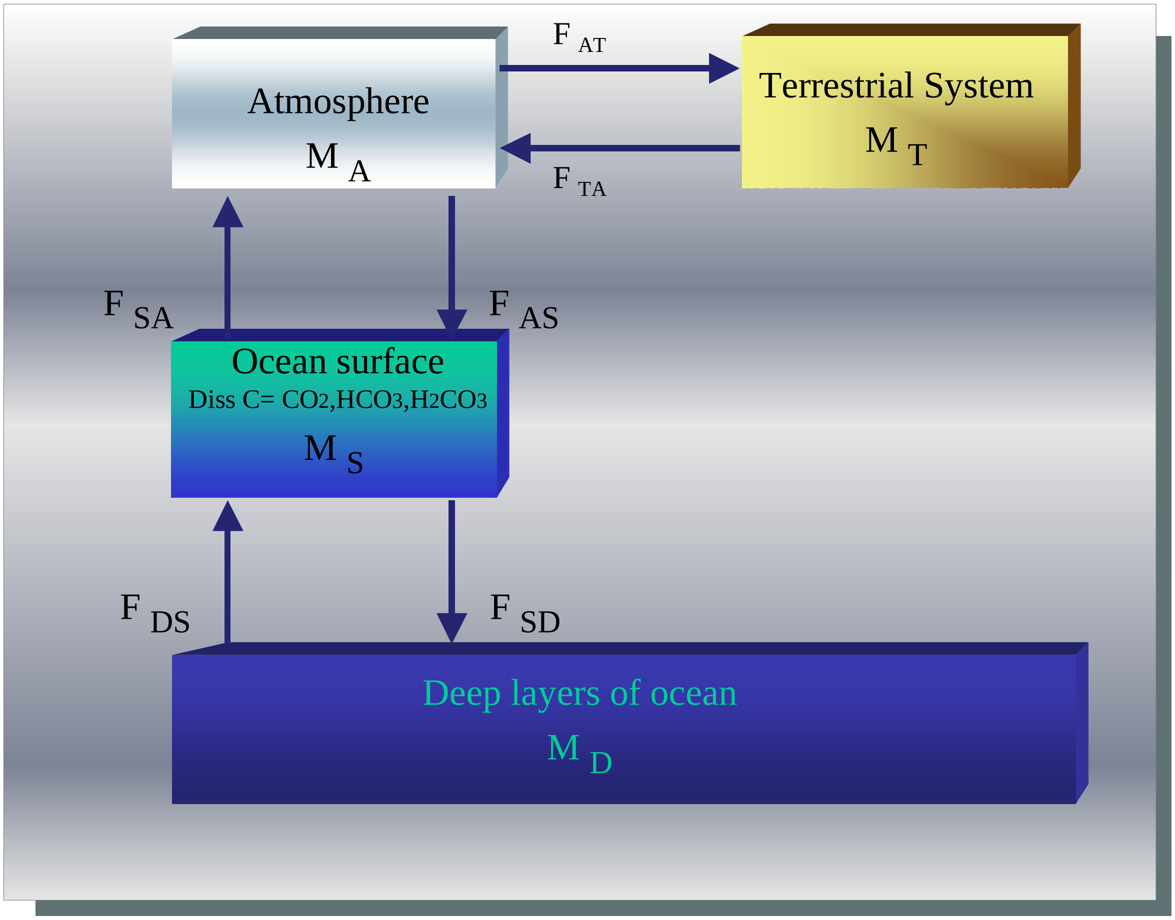

Figure 7. A Simplified Model of the Carbon Cycle

3. Inorganic Carbon Cycle

The inorganic carbon cycle involves the carbon exchange between the ocean and the atmosphere, chemical weathering and carbonate and silicate mineral deposition. This is depicted in Figure 8.

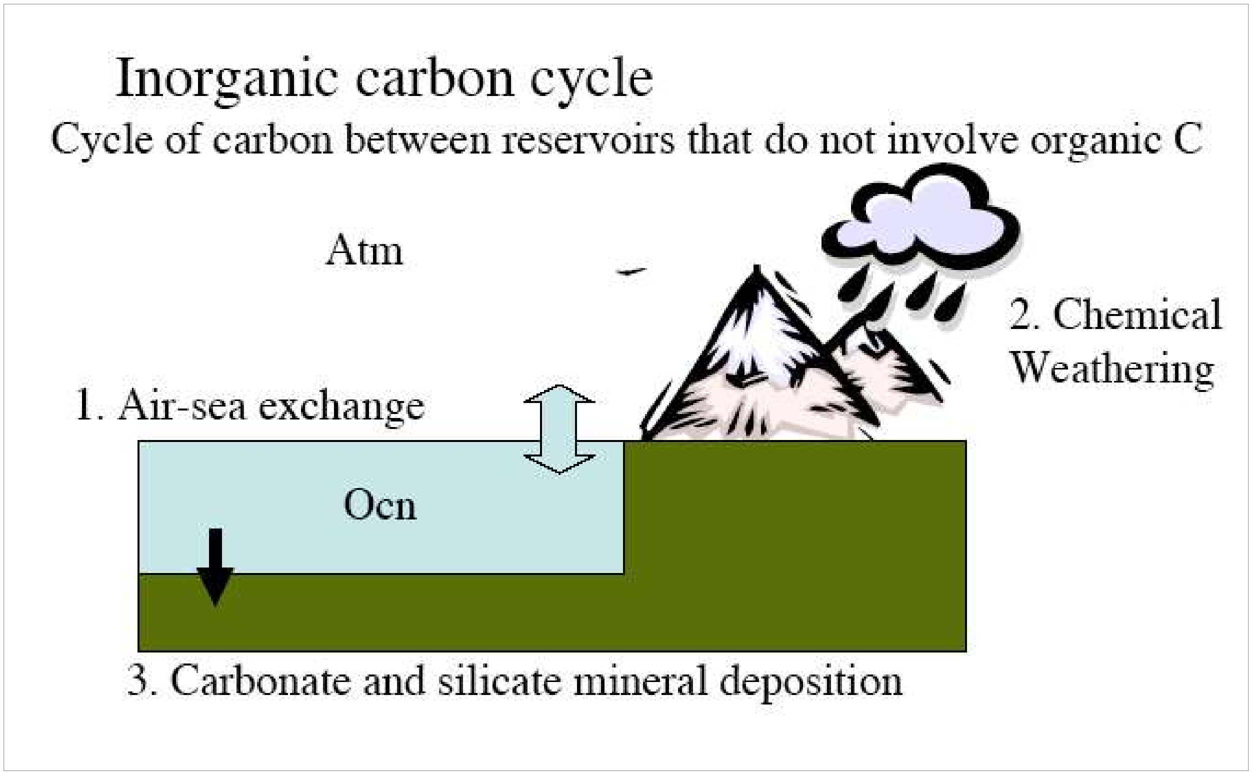

Figure 8. The Inorganic Carbon Cycle

3.1 Carbon Exchange Between the Atmosphere and the Ocean

The first step in the exchange of carbon between the atmosphere and the ocean is the *diffusion* of atmospheric carbon dioxide (CO_2), as well as oxygen gas (O_2) on the surface of the ocean. It is then *dissolved* and reacts with water to form *carbonic acid* ($H_2CO_3^*$). This is reaction is shown in equation (13) below.

$$CO_2 + H_2O \leftrightarrow H_2CO_3^* \qquad (13)$$

This is a reversible process in which the start of the reaction depends on which side has a larger concentration. The reaction reaches *equilibrium* and the concentrations become constant.

The next step is that carbonic acid further breaks down into a hydrogen ion (H^+) and into a *bicarbonate* ion (HCO_3^-) as shown below in equation (14).

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \tag{14}$$

Bicarbonate is then further decomposed to another hydrogen ion and a *carbonate* ion (CO_3^{2-}). This is depicted in the chemical equation below.

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \tag{15}$$

The equilibrium relationships between these chemical species are given by the following equations below:

$$K_0 = \frac{\left[H_2CO_3^*\right]}{pCO_2} \tag{16}$$

$$K_1 = \frac{\left[H^+\right]\left[HCO_3^-\right]}{\left[H_2CO_3^*\right]} \tag{17}$$

$$K_2 = \frac{\left[H^+\right]\left[CO_3^{2-}\right]}{\left[HCO_3^-\right]} \tag{18}$$

where *pCO_2* is the partial pressure of CO_2 and the quantities inside the [ ] are concentrations. Equilibrium between carbon dioxide, carbonate ion and bicarbonate ions in the ocean water is the *overall effect*. This is depicted in equation (19). This means that the capacity of the ocean to absorb carbon dioxide in the atmosphere does not only depend on the dissolved carbon dioxide in ocean water since the dissolved carbon dioxide is transformed to other forms of inorganic carbon.

$$CO_2 + CO_3^{2-} + H_2O \leftrightarrow 2HCO_3^- \tag{19}$$

A necessary concept for the exchange of carbon between the atmosphere and the ocean is *acidity*. In essence, acidity refers to the concentration of hydrogen ions in a solution. More hydrogen ions means a more acidic solution while less hydrogen ions means a more basic solution. A measure of acidity is the *pH* where

$$pH = -\log\left[H^{+}\right] \tag{20}$$

A solution with a pH value of less than 7 is called an acid, a solutions with a pH value of greater that 7 is called a base and a solution with a pH value of exactly 7 is called a neutral solution. In relation to the previous discussion, more acidic ocean water tends to favor bicarbonate ions than carbonate ions as shown in Figure 9. It can also be noticed that the current pH value of the ocean is around 8.

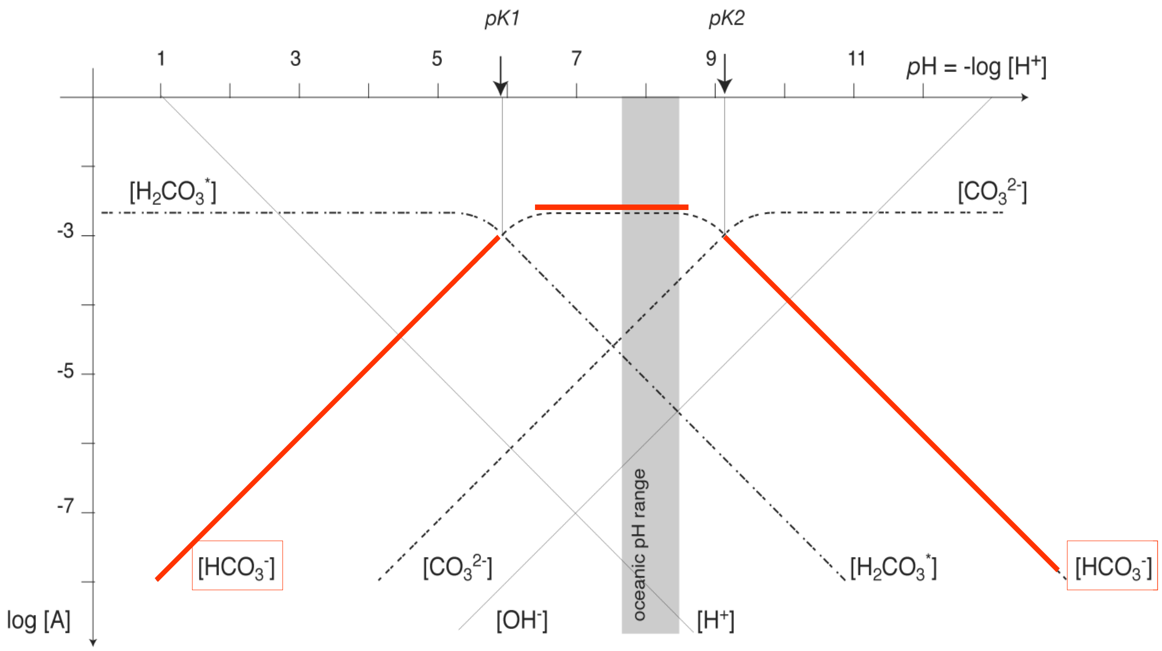

Figure 9. Concentration of Chemical Species as a Function of pH

3.2 Chemical Weathering of Rocks

There are two types of chemical weathering of rocks. One is called *carbonate weathering* and the other is called *silicate weathering*. In both cases, the process begins with the production of carbonic acid, in this case, when rainwater reacts with carbon dioxide in the atmosphere in as much the same way ocean water dissolves atmospheric carbon dioxide as discussed in the previous section.

For carbonate weathering, *limestone* or *calcium carbonate* ($CaCO_3$) reacts with carbonic acid and produces a calcium ion and bicarbonate ion as expressed by

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- \tag{21}$$

For silicate weathering, *wollastonite* ($CaSiO_3$) reacts with carbonic acid forming a calcium ion, bicarbonate ions, silica (SiO_2) and water as given by

$$CaSiO_3 + 2H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- + SiO_2 + H_2O \tag{22}$$

3.3 Carbonate and Silicate Mineral Deposition

Minerals from weathering are transported to the ocean where organisms take up calcium and bicarbonate in the water to form calcium carbonate for shells and skeletons (phytoplanktons and zooplanktons). When these organisms die, they sink and the calcium carbonate does not dissolve in shallow oceans. This means that calcium deposits are found more in mid-ocean ridges where the ocean is shallow as depicted in Figure 10.

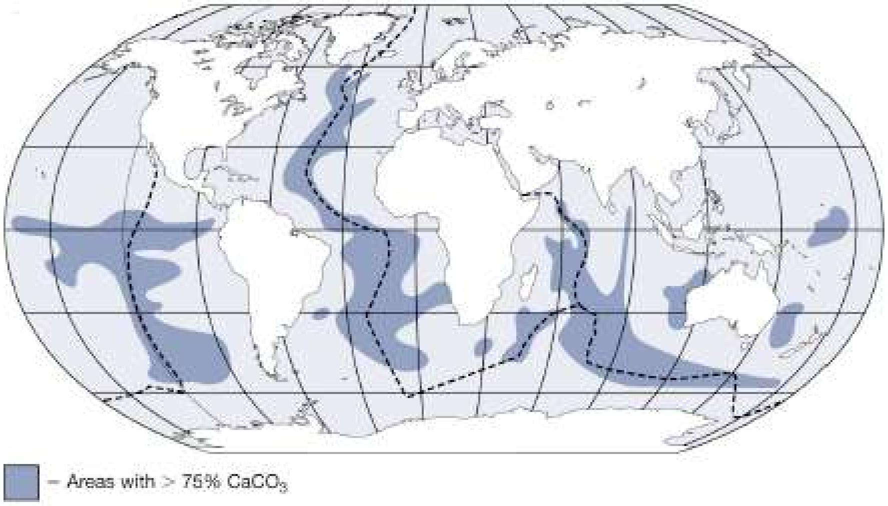

Figure 10. Calcium Deposits

4. Organic Carbon Cycle

The organic carbon cycle involves a *short-term* and a *long-term* process. The short-term organic carbon cycle involves *photosynthesis* and *respiration*. Photosynthesis takes up carbon dioxide in the atmosphere and involves water and sunlight as well producing living tissue and oxygen. This is expressed by the chemical reaction

$$CO_2 + H_2O \rightarrow CH_2O + O_2 \tag{23}$$

Respiration or decay, on the other hand, is exactly the opposite of photosynthesis as given by

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \tag{24}$$

The long-term organic carbon cycle deals with the burying of organic material and not undergoing the decay process. These materials are then incorporated as *fossil fuels*.